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OPTIMIZATION OF TECHNOLOGICAL PARAMETERS IN THE PRODUCTION OF VITREOUS COATINGS FROM GLASS-FORMING COLLOID SOLUTIONS

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The effect of the physicochemical properties of glass-forming colloid solutions (GCS) and of technological parameters on the production of vitreous coatings for steel is investigated. The optimum conditions for GCS deposition and fusion of the products of thermal deposition of GCS, which are synthesized on the basis of TEOS and nitrates of monovalent and bivalent metals, are developed.

The high requirements imposed on the quality and reliability of enameled metal products call for upgrading of this production technology. This can be facilitated by the development of new compositions for enamel coatings and introduction of state-of-the-art enameling techniques (sol-gel process, plasma spray deposition, etc.) [1, 2].

In contrast to the traditional enameling scheme, in which the technological parameters insignificantly vary depending on the composition and type of enamel (vitreous coating), in using the sol-gel method, one has to develop a specific technology for each specific composition of glass-forming colloid solution (GCS).

The difficulty in making vitreous coatings from GCS lies in the need to take into account the dynamic variations of the physicochemical properties of such solutions in time [3]. Furthermore, the technological regime (deposition and fusion parameters) also plays an important role in ensuring good adhesion of such heterogeneous materials as glass and metal. Therefore, to solve the problem of making high-quality coatings from GCS, a multilateral approach is needed.

The purpose of the present study was to reduce the great number of technological parameters to the optimum ones and to use them in the synthesis of thin vitreous coatings for steel from GCS. The technological parameters are understood as the deposition parameters (flow characteristics, time and number of deposition cycles, temperature of the steel substrate, temperature and exposure duration of thermal precipitation products) and the fusion parameters.

A glass-forming colloid solution was synthesized on the basis of hydrolyzed TEOS and nitrates of calcium, lithium, manganese, copper, and boric acid. After the obtained solution was deposited by pulverization and the precipitation products were fused on the steel substrate, the following vitreous coating was obtained (wt.%): 60.0 SiO_2, 10.0 CaO, 30.0 Li_2O, 6.0 B_2O_3, 3.2 MnO, and 2.8 CuO.

It was shown earlier [4] that the developed GCS in its properties satisfies the requirements imposed on a coating for steel (its dynamic viscosity does not exceed 10 Pa · sec over a period of 14 days). One of the main criteria for getting a high-quality coating in this case is the temperature of the substrate. In GCS deposition by pulverization on a substrate (steel Kh149900P) heated up to 400°C, it is difficult to obtain a uniformly distributed, continuous layer of thermally deposited products with sufficient thickness. An increase in pulverization duration leads to sagging of the solution.

The best and the densest layer of thermal deposition products was obtained when the substrate temperature was 400 – 500°C. An increase in the temperature above the specified values results in the deposition of coarsely dispersed powder, and it is hard to obtain a continuous vitreous coating through the fusion of such powder, owing to numerous defects ("fish scales," etc.). The duration of GCS spraying on a substrate heated to the optimum temperature was determined visually and amounted to 10 – 12 sec. It should be noted that the temperature of the substrate and the duration of GCS spraying are effective parameters for controlling the thickness of the glass coating. The drying temperature (170°C) was determined based on the DTA data. The drying duration was determined experimentally and was equal to 10 min.

In order to determine the GCS concentration suitable for getting a high-quality vitreous coating, solutions with varying degrees of dilution (1, 2, 4, 6, 8, and 10%) were prepared. Microscopic studies and measurements of the glass-coating thickness indicated that the solutions with 4 – 8% content of GCS in the case of two-time deposition and fusion are suitable as protective materials for steel.

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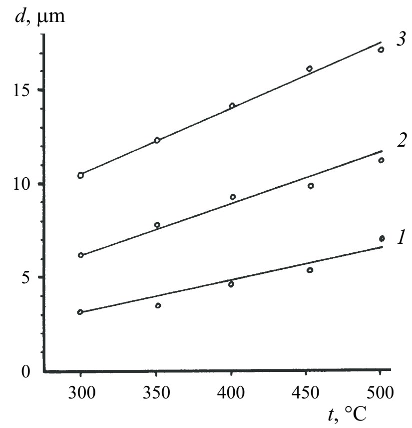

Fig. 1. Dependence of the thickness d of the vitreous coating on the temperature t of the steel substrate with viscosity 1.32 (*1*), 1.91 (*2*), and 2.76 Pa · sec (*3*).

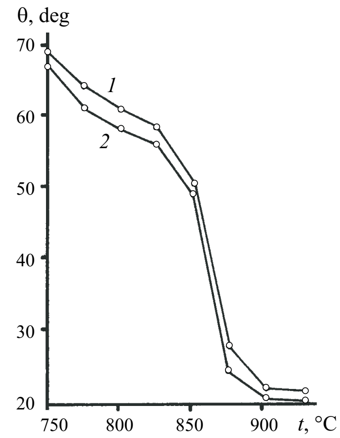

Fig. 2. Dependence of the contact angle of wetting θ of steel substrate on temperature t in holding for 2 (*1*) and 3 min (*2*).

The method of depositing GCS by pulverization is best used in articles of simple geometrical shape. One of the methods for applying a vitreous coating on an article with a complex shape is immersion [5]. The quantity of the thermal deposition products in this case depends on the temperature of the article and the flow parameters of the GCS. The main parameters developed for this regime include the temperature, the metal substrate (article) heating duration, and the exposure of the article in the GCS.

The determination of the functional relationship between the vitreous-coating thickness (a DM 100 device) and the substrate temperature was carried out under variable dynamic viscosity of the GCS (a VPZh-2 viscosimeter). Analyzing the obtained data (Fig. 1), it can be inferred that the glass-coating thickness is proportional to the substrate temperature. As the sample temperature grows from 300 to 500°C, the glass coating thickness increases by 3 – 5 μm. It should be noted that the GSC viscosity has a more significant effect on the coating thickness. A vitreous coating made of GCS with 2.76 Pa · sec viscosity is 3 times thicker than a coating made of a solution with a viscosity of 1.32 Pa · sec, the substrate temperatures being equal. By modifying these technological parameters, it is possible to control the thickness of the vitreous coating with a great degree of precision.

The optimum fusion mode was developed on the basis of measuring the wetting angle of the substrate (a KM-8 cathetometer) and the adhesion of the glass coating to the substrate (GOST 24-788–81). One of the main conditions for the adhesion of a vitreous coating to metal is good wettability of the substrate with the glass melt. The contact wetting angle θ reaching the equilibrium value is the measure of the wetting ability of the glass melt. The determination of the temperature dependence of θ would make it possible to select the temperature interval for the formation of a vitreous coating more objectively.

TABLE 1

Fusion temperature, °C (Δ = ± 2°C)	Adhesion, % (Δ = ± 0.5%)	Wetting angle, deg (Δ = ± 0.5°)
750	66	67
775	68	60
800	71	58
825	74	55
850	76	48
875	78	23
900	75	20
925	69	20

To determine the value of θ, glass granules (their composition was identical to the composition of the glass coating) of equal weight made by the traditional technology were placed on steel substrates and heated in a muffle furnace at different temperatures and different exposures (Fig. 2). Since the surface tension of glass does not change in cooling, in contrast to the glass viscosity [6], it can be assumed that the shape of a glass drop (its height and base diameter) does not vary significantly, which makes it possible to determine θ after cooling of the glass. The shape of the curves exhibits a smooth decrease in the values of θ as the temperature increases up to 850°C. One should note the insignificant difference in the values of θ as the exposure grows from 2 to 3 min (1 – 2°). Starting with a temperature of 850°C or more, the parameter θ sharply decreases and acquires a constant minimum value within the temperature interval of 890 – 925°C. The constant value of θ in this interval should be considered a positive factor, since no possible deviations in the temperature conditions in fusion will affect the quality of the product. Taking into account the sharp decrease in θ at a temperature of 850°C, it can be assumed that the chemical reaction between glass and metal starts at this temperature.

It was impossible to identify a correlation between wetting and adhesion in the course of the study (Table 1). The adhesion values continuously grow up to a temperature of 875°C and then decline, whereas the curves in Fig. 2 indicate the maximum spreading at temperatures of 890 – 925°C. Therefore, wetting should be regarded only as a factor ensur-

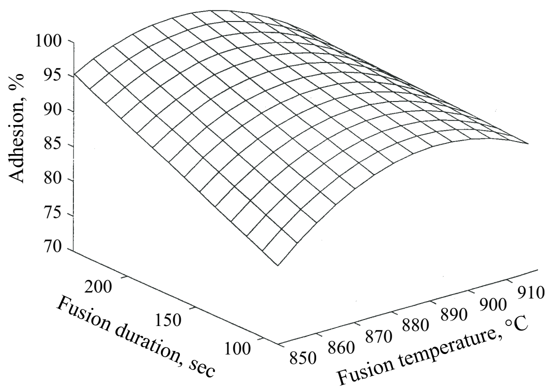

Fig. 3. Response surface.

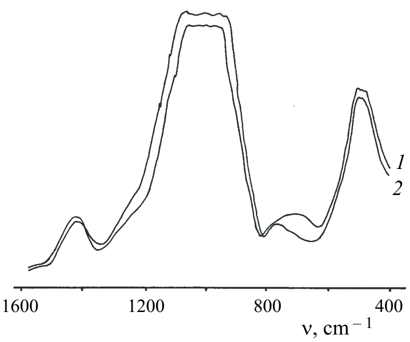

Fig. 4. IR absorption spectra of glasses obtained from GCS (*1*) and crystalline material (*2*).

ing uniform distribution of the glass melt over the metal surface.

The search for the optimum fusion conditions included a mathematical design of experiment. The value of adhesion served as the criterion to evaluate the completeness of the fusion processes. The selected variables were temperature X_1 and duration X_2 of glass-coating fusion, and the response function Y was the surface area of the glass coating that remained on the steel surface after the measurement of the adhesion value.

A center-composition design of experiment (the orthogonal variety) was selected for an adequate mathematical description of the process. Computerized calculations produced a regression equation, which relates adhesion to the technological parameters of the fusion of the vitreous coating:

$$Y = (-4871.0 \pm 22.6) + (11.0 \pm 1.0)X_1 +$$
$$(1.2 \pm 0.3)X_2 - (0.01 \pm 0.002)X_1X_2 - (0.06 \pm 0.002)X_1X_2.$$

The analysis of the response surface (Fig. 3) shows that as the fusion duration grows, the adhesion of vitreous coating to metal increases linearly and insignificantly. The dependence of adhesion on the fusion temperature is more complex. This function has an extremum at 875°C. While the temperature is below the optimum value, the reaction between glass and metal at the phase boundary does not proceed to a full measure. Heat treatment at higher temperatures (900°C) apparently results in the formation of a thick scale layer, which impairs the adhesion.

This poses the question whether the vitrification processes in the batch mixture have fully taken place in fusion during such a short period (up to 4 min). Contrary to the traditional enamels, in which the coating production consists of the fusion of disperse glass powder, in which the vitrification has been completed, the process of salt decomposition, vitrification, and adhesion to the substrate in the products of thermal precipitation of GCS under heat treatment (fusion) occur simultaneously, which could require higher temperatures or longer heat-treatment duration.

A comparison of the IR absorption spectra of glass produced from the thermal-deposition products at a temperature of 875°C and a 3-min exposure and those of glass of a similar composition made from the batch (quartz sand, lithium and calcium carbonates, boric acid) according to the standard technology (melting in a corundum crucible at 1450°C and 2-h exposure) suggests that both glasses have a similar structure (Fig. 4).

The position of the band with the maximum at 800 cm^{-1} is slightly shifted toward the low-frequency region, and its intensity is higher in the glass made of GCS. The presence of this band caused by joining of $[SiO_4]^{4-}$ tetrahedrons and its shape indicate that in the glass made of GCS, silicon-oxygen chains of different length participate to a greater degree in structure formation. An x-ray phase analysis confirms the completion of the silicate formation process. The diffraction patterns of the glass obtained from the products of GCS thermal deposition do not exhibit crystalline compounds in the ranges of angles $2\theta = 16 - 36°$.

The systematic approach implemented in the development of vitreous-coating production technologies made it possible to determine the optimum values of the sought technological parameters. The most significant factors affecting the production of high-quality continuous protective glass coatings for steel are the concentration and the viscosity of GCS. It can be assumed that these parameters should lie within certain limits, regardless of the GCS composition.

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